

THE VISCOUS SLOWING DOWN OF SUPERCOOLED LIQUIDS AND THE GLASS TRANSITION: PHENOMENOLOGY, CONCEPTS, AND MODELS

G. TARJUS

Laboratoire de Physique Théorique des Liquides, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris cedex 05, France

D. KIVELSON

Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095, USA

Abstract

The viscous slowing down of supercooled liquids that leads to glass formation can be considered as a classical, and is assuredly a thoroughly studied, example of a "jamming process". In this review, we stress the distinctive features characterizing the phenomenon. We also discuss the main theoretical approaches, with an emphasis on the concepts (free volume, dynamic freezing and mode-coupling approximations, configurational entropy and energy landscape, frustration) that could be useful in other areas of physics where jamming processes are encountered.

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I. INTRODUCTION

When cooling a liquid, usually under isobaric $P=1\text{atm}$ conditions, one can often bypass crystallization, thereby obtaining a supercooled liquid that is metastable relative to the crystal. When the temperature is further lowered, the viscosity of the liquid, as well as the relaxation times associated with the primary (α) relaxation of all kinds of structural, dielectric, macro- and micro-scopic observables, increase rapidly, until a temperature is reached at which the liquid can no longer flow and equilibrate in the time scale of the experiment. The system effectively appears as a rigid amorphous material and is then called a glass. Glass formation thus results from the strong viscous slowing down of a liquid with decreasing

temperature¹, a slowing down that can be considered as a classical example of a “jamming process”. A characteristic of this process that is unanimously recognized, a unanimity rare in this otherwise quite open and controversial field, is that it is a dynamic effect. The so-called “glass transition” is not a *bona fide* thermodynamic phase transition, but represents a crossover below which a liquid falls out of equilibrium on the experimental time scale. The transition temperature, T_g depends on this time scale, set either by the observation time (corresponding, for instance, to a relaxation time of 10^2 or 10^3 sec or a viscosity of 10^{13} Poise) and/or by the cooling rate (in a typical differential scanning calorimetry measurement, 10 K per minute). The dependence on cooling rate is, however, weak, a difference of few K in T_g for an order-of-magnitude change of the rate; this is so because on further lowering of the temperature the viscosity and α -relaxation times rapidly become enormous and out of reach of any experimental technique.

In the following, we shall focus on the jamming process occurring in the supercooled liquid state. [1,2] Both the crystal², which is the stable phase below the melting point T_m but can be ignored in discussing the glass transition, and the glassy state itself will be excluded from the present discussion. By appropriately eliminating the crystal (experimentally as well as theoretically), metastable supercooled liquids can be treated by equilibrium thermodynamics, statistical mechanics, and conventional linear-response formalisms. Glasses on the other hand, although mechanically stable, are out-of-equilibrium states; especially near T_g , they display nonlinear responses and relaxations known as aging or annealing, and their properties depend on their history of preparation. [4,5] These phenomena will not be considered in this review.

II. SALIENT PHENOMENOLOGY

The distinctive feature of glass-forming liquids is the dramatic, continuous increase of viscosity and α -relaxation times with decreasing temperature. This sort of jamming is observed in a large variety of substances: covalently bonded systems like SiO_2 , hydrogen-bonded liquids, ionic mixtures, polymers, colloidal suspensions, molecular van der Waals liquids, etc. The emphasis will be placed on those liquids (the vast majority) that do not form 2- or 3-dimensional networks of strong bonds because they show the most striking behavior when passing from the high-temperature liquid phase to the deeply supercooled and very viscous regime.

¹Although not as widely used, there are other ways of generating glassy structures, such as vapor deposition, in situ polymerization or chemical reactions. [3]

²Note that for several liquids, such as m-fluoroaniline and dibutylphtalate at atmospheric pressure and atactic polymers, crystallization has never been observed.

1. Strong, super-Arrhenius T-dependence of viscosity and α -relaxation times

The viscosity η and α -relaxation times can change by 15 orders of magnitude for a mere decrease of temperature by a factor two³. Such a dramatic variation is conveniently represented on a logarithmic plot of η or τ_α versus $1/T$, i.e., an Arrhenius plot: see Fig. 1a. A system like GeO_2 , an example of a network-forming system, is characterized by an almost linear variation, which indicates an Arrhenius temperature dependence. For all other liquids on the figure there is a marked upward curvature, which represents a faster-than-Arrhenius, or super-Arrhenius, temperature dependence and is often described by an empirical Vogel-Fulcher-Tammann (VFT) formula (also called Williams-Landel-Ferry formula in the context of polymers studies [6]),

$$\tau_\alpha = \tau_0 \exp \left(D \frac{T}{T - T_0} \right), \quad (1)$$

where τ_0 , D and $T_0 < T_g$ are adjustable parameters. On the basis of such Arrhenius plots, with the temperature scaled by T_g , Angell proposed the now standard classification of glass-forming liquids into *strong* (Arrhenius-like) and *fragile* (super-Arrhenius) systems; [7] in Eq. (1), the smaller the value of D , the more fragile the liquid. There are, of course, alternative fitting formulas that have been used, some which do not imply a singularity at a nonzero temperature as does the expression in Eq. (1). [8]

A different way of representing the phenomenon is to plot the effective activation free energy for α -relaxation, $E(T)$, obtained from

$$\tau_\alpha = \tau_{\alpha,\infty} \exp \left(\frac{E(T)}{k_B T} \right), \quad (2)$$

where k_B is the Boltzmann constant and $\tau_{\alpha,\infty}$ is a high- T relaxation time, or from a similar equation for the viscosity. This is illustrated in Fig. 1b, where the temperature has been scaled for each liquid to a temperature T^* above which the dependence is roughly Arrhenius-like. Although the determination of T^* is subject to some uncertainty, [8,9] the procedure emphasizes the crossover from Arrhenius-like to super-Arrhenius behavior that is typical of and quite distinct in most supercooled liquids. The appreciable size of the effective activation free energies $E(T)$, namely, $40k_B T_g$ at the glass transition, is indicative of thermally activated dynamics. Such a large effective activation free energy for weakly bonded fragile molecular liquids such as orthoterphenyl is an intriguing feature of the phenomenology. Another peculiar property of $E(T)$ for fragile systems is that it increases significantly between T^* and T_g (a factor 3, i.e., a factor of 5 or 6 in units of the thermal energy $k_B T$, for weakly bonded fragile liquids). Such a variation is not commonly encountered. For instance, in the field of critical phenomena, the slowing down of dynamics that occurs when approaching the

³The (shear) viscosity η can be related to a time characteristic of α -relaxation, the average shear stress relaxation time τ_s , by $\eta = G_\infty \tau_s$, where G_∞ is the infinite-frequency shear modulus; G_∞ is typically of the order of $10^{10} - 10^{11}$ erg.cm⁻³, so that a viscosity of 10^{13} Poise roughly corresponds to a time of 10^2 or 10^3 sec.

critical point is usually characterized by a power law growth of the relaxation time; in terms of effective activation free energy, this corresponds to a logarithmic growth and it is slower than the variation described by the VFT formula, Eq. (1). Unusually strong slowing down, with exponentially growing times similar to Eq. (1), is found in some disordered systems like the random field Ising model and it is known as “activated dynamic scaling”. [10]

2. Nonexponential relaxations

In an “ordinary” liquid above the melting point, relaxation functions are usually well described, after some transient time, by a simple exponential decay. Deviations are observed, but they are neither systematic nor very marked. The situation changes at lower temperatures, and the α -relaxation is no longer characterized by an exponential decay. A better representation is provided by a “stretched exponential” (or Kohlrausch-Williams-Watts function),

$$f_\alpha(t) \propto \exp \left[- \left(\frac{t}{\tau_\alpha} \right)^\beta \right], \quad (3)$$

where β is the stretching parameter; the smaller β the more “stretched” the relaxation. Although not unambiguously established, the degree of departure from exponential behavior, or stretching, appears to increase (i.e., β decreases) with decreasing temperature.

Alternatively, in frequency space, the spectrum of the imaginary part of the susceptibility, which is characterized by a peak at a frequency $\omega_\alpha \propto 1/\tau_\alpha$, tends to be broader (when plotted as a function of $\log(\omega)$) than the simple Lorentzian or Debye spectrum that is just the Fourier transform of the time-derivative of an exponential relaxation function (see Fig. 2). Fitting formulas related to Eq. (3), formulas like the Cole-Davidson function for frequency-dependent susceptibilities, $(1 - i(\omega/\omega_\alpha))^{-\beta'}$, are used to fit the spectroscopic data, but similar trends are observed: the α peak, as observed for instance in the imaginary part of the dielectric susceptibility as a function of $\log(\omega)$, broadens as the temperature is lowered towards T_g , [11] which indicates increasing departure from Debye/exponential behavior. Except for network-forming systems, the stretching of the α relaxation is significant (β is typically between 0.3 and 0.6 for fragile liquids at T_g). However, and this point may not have been given enough attention, the stretching, or broadening in frequency space, is relatively small when compared to the extremely rapid variation with temperature of the α -relaxation time itself. This is to be contrasted for instance with the activated critical slowing discussed above. There, the power law growth of the activation free energy when the temperature is decreased toward the critical point comes with a more striking stretching of the relaxation function that occurs on a logarithmic scale: in this case, in place of a stretched exponential behavior as in Eq. (3), $\ln(f(t))$ goes as some power of $(1/\ln(t))$. [12]

3. No marked changes in structural quantities

It is tempting to associate the huge increase in α -relaxation times and viscosity with the growth of a *structural* correlation length. However, no such growth has been detected so far in supercooled liquids. Quite to the contrary, the variation of structure in liquids and glasses,

as measured in neutron and X-ray diffraction experiments, appear rather bland [13,14] (see Fig. 3). The ordinary, high-temperature liquid has only short-range order whose signature in the static structure factor $S(Q)$ is a broad peak (or a split peak for some molecular systems as illustrated in Fig. 3) at a wave vector Q that roughly corresponds in real space to some typical mean distance between neighboring molecules. As the temperature is lowered and the supercooled regime is entered, there are small, continuous variations of the structure factor that mostly reflect the change in density (typically, a 5% change between T_m and T_g) and, possibly, some adjustments in the local arrangements of the molecules. There is no sign, however, of a significantly growing correlation length, nor of the appearance of a super-molecular length.

In network-forming and H -bonded systems, an additional “pre-peak” is sometimes detectable at wave vectors somewhat lower than that of the main peak, but it is attributed to specific effects induced by the strongly directional intermolecular bonds and not to a length scale that would correlate with the viscous slowing down. [15]

In contrast to this lack of structural signature for the existence of an increasing super-molecular correlation length with decreasing temperature, there is significant evidence, as discussed below, that corresponding “dynamical” correlation length do exist.

4. Rapid entropy decrease and Kauzmann paradox

The absence of marked changes in the structure, *at least at the level of two-particle density correlations*, or of a strong increase in any directly measured static susceptibility is a puzzling feature of the jamming process associated with glass formation. The only static quantity that shows behavior that might be relevant is the entropy. Below the melting point, T_m , the heat capacity $C_p(T)$ of a supercooled liquid is larger than that of the corresponding crystal. (At T_g , the C_p of the liquid drops to a value that is characteristic of the glass and is close to the C_p of the crystal, but this is a consequence of the system no longer being properly equilibrated.) As a result of this “excess” heat capacity, the entropy difference between the liquid and the crystal decreases with temperature, typically by a factor of 3 between T_m and T_g for fragile liquids. The effect is illustrated in Fig. 4 and leads to the famous Kauzmann paradox: [16] if the entropy difference is extrapolated to temperatures below T_g , its extrapolated value vanishes at some nonzero temperature T_K , which results in the unpleasant feature that the entropy of the liquid becomes equal to that of the crystal (even more unpleasant: if the extrapolation is carried to still lower temperatures, the entropy of the liquid becomes negative, which violates the third law of thermodynamics). The paradox is that this *extrapolated* entropy crisis is avoided for a purely dynamic reason, the intervention of the glass transition: what would occur if one were able to keep the supercooled liquid equilibrated down to temperatures below T_g ? There are certainly many ways to answer the question. The paradox could be resolved by the existence between T_g and T_K of an intrinsic limit of metastability of the liquid [16] or of a second-order phase transition⁴ (a speculation

⁴Note that a low- T first-order transition does not resolve the paradox because it can be supercooled.

that gains additional credibility with the observation that the VFT temperature T_0 at which the extrapolated viscosity and α -relaxation times diverge (see Eq. (1)) is often found close to T_K [17,18]). Even more simply, one might find that the extrapolation breaks down above T_K and that the entropy-difference curve levels off and goes smoothly to zero at zero K , in much the same way as it does in the Debye theory of crystals. These are of course all speculations, but it remains that the rapid decrease of the entropy of the supercooled liquid relative to that of the crystal represents an intriguing aspect of the phenomenology of fragile glass-formers.

5. Two-step relaxation and secondary processes

As we stressed before, the salient features related to glass formation concern the long-time (low-frequency) primary or α relaxation. As the α -relaxation time increases with decreasing temperature, so too does the window between this time and typical microscopic, picosecond or sub-picosecond times. When the relaxation function is plotted against the logarithm of the time, one then observes what is sometimes called a “two-step relaxation”. An illustration is given in Fig. 5 by the dynamic structure factor of the fragile ionic glass-former $Ca_{0.4}K_{0.6}(NO_3)_{1.4}$ obtained by neutron techniques. [19] At high temperature, the relaxation function is essentially a one-step process. However, as the liquid becomes more viscous, the relaxation proceeds in two steps separated by a plateau. Although the terminology is far from being universally accepted, the approach to the plateau from the short-time side is often referred to as β or fast- β relaxation. If one is to fit the long-time part by a stretched exponential (Eq. (3)), there is a large range of “mesoscopic” times that is not adequately described and that widens as the temperature is lowered. Power law functions of time are often used to reproduce the relaxation function in this mesoscopic range.

This two-step relaxation feature is common to all fragile liquids. In addition, there may also appear additional secondary processes, detected first by Johari and Goldstein in dielectric spectroscopy. [20] Such secondary processes, whose presence and strength strongly vary from one liquid to another, have characteristic frequencies that are intermediate between those of the α and fast- β relaxations. They are denoted Johari-Goldstein- β , slow- β , or simply β processes. [2,21] To make the description more complete, one should also mention the so-called “boson peak” that may be present on the high-frequency side ($\sim 10^2 - 10^3 GHz$) of light and neutron scattering (or absorption) spectra. [2,22] Here we do not discuss either the slow- β processes or the boson peak.

III. A SELECTION OF QUESTIONS

After this brief review of the salient aspects of the phenomenology of supercooled liquids as they get glassy, we discuss in more detail a number of questions, whose answers give justification or put constraints on the theoretical picture one can build to explain the viscous slowing down.

1. How universal is the behavior of glass-forming liquids ?

Universality is a key concept in physics and it has proven to be central in the field of critical phenomena. By the standards of critical phenomena studies, the observed behavior of glass-forming liquids is not universal, the main reason being that no singularity is detected experimentally (or approached asymptotically close), as stressed above. However, if one is willing to take a broader view of the notion of universality, one can find considerable generality or “universality” in the properties, those mostly associated with long-time and low-frequency phenomena, that characterize the approach to the glass transition. For instance, the super-Arrhenius T -dependence of the viscosity and α -relaxation times and the nonexponential character of the relaxation function are observed for virtually all glass-formers, be they polymeric, H -bonded, ionic, van der Waals, etc., with the exception of a minority of strong network-forming systems; and, for a given liquid, these properties are found by a large variety of experimental techniques, such as dielectric relaxation, light and neutron scattering, NMR, viscosity measurements, specific heat spectroscopy, volume and enthalpy relaxation, optical probe methods.

The presence of an underlying “universality” is supported by the fact that experimental data covering a wide range of temperatures and a great diversity of substances can be collapsed onto master curves with only a small number of species-dependent adjustable parameters. A good example is provided by the scaling plot of the frequency-dependent dielectric susceptibility proposed by Nagel and coworkers. [11] As shown in Fig. 6, the data taken over a 13 decade range of frequencies for many different liquids can be placed with good accuracy onto a single curve after scaling with only three parameters associated with the α -peak position, width and intensity. The master-curve for the temperature dependence of the effective activation free energy for viscosity and α relaxation put forward by Kivelson *et al.* [8] is another example. It is nonetheless fair to say that the fits resulting from these various scaling procedures are far from perfect, which leaves room for debate and conflicting interpretations. One can also ask the question whether the universality holds only up to the implied high-frequency cut-off of the susceptibility scaling curve of Nagel *et al.* (i.e., whether one should be focusing on slow behavior) or whether it extends higher in light of the fact that similarities have also been observed in the high-frequency susceptibilities. [23]

2. Is the α -relaxation homogeneous or heterogeneous?

The observation stressed above that the α -relaxation is nonexponential in the supercooled liquid range and its representation by a stretched exponential as in Eq. (2) can be formally interpreted in terms of a superposition of exponentially decaying functions with a distribution of relaxation times; but, this *per se* does not guarantee that the dynamics be “heterogeneous”, in the sense that relaxation of the molecules differs from one environment to another with the environment life time being longer than the relaxation time. An alternative explanation can be offered within a “homogeneous” picture in which relaxation of the molecules everywhere in the liquid is intrinsically nonexponential.

In recent years, there has been mounting evidence that heterogeneities, sufficiently long-lived to be relevant to the α -relaxation and to be at least partly responsible for its nonexponential feature, do exist in supercooled liquids. [24] The heterogeneous character of the

slow dynamics has been demonstrated in several experiments: multi-dimensional NMR, [25] photobleaching probe rotation measurements, [26] nonresonant dielectric hole burning. [27] These techniques involve the selection of a sub-ensemble of molecules in the sample that is characterized by a fairly narrow distribution of relaxation times (and in general a relaxation slower than average) and the further monitoring of the gradual return to the equilibrium situation. Additional evidence of the spatially heterogeneous nature of the dynamics in fragile supercooled liquids is provided by the so-called breakdown of the Stokes-Einstein relation between the translational diffusion constant and the viscosity, and the concomitant “decoupling” between rotational and translational time scales: [28,29] see Fig.7.

The size of the heterogeneities is not directly observable in the above mentioned experiments, but various estimates, obtained, e. g., from optical studies of the rotational relaxation of probes of varying size, [30] NMR measurements, [31] the study of excess light scattering, [32] and the influence of a well-defined 3-dimensional confinement [33] lead to a typical length of several nanometers in different fragile liquids near T_g . One should recall that these signatures are all dynamical and that no signature at such a length scale has been detected so far in small-angle neutron and X-ray diffraction data. If the heterogeneous character of the α -relaxation appear reasonably well established, at least for deeply supercooled fragile liquids, several points concerning the lifetime, the size, and the nature of the heterogeneities need still be settled.

3. Is density or temperature the dominant control variable?

The phenomenon of viscous slowing down and glass formation as it is studied most of the time (and described in the preceding sections) takes place under isobaric $P = 1 atm$ conditions. As a consequence, when the temperature is lowered, there is also an increase of the density of the liquid. This increase is small (a typical variation of 5% between T_m and T_g), but it could still have a major influence on the dynamics. Actually, there are theoretical models of jamming, such as those based on free volume concepts and hard sphere systems, that attribute the spectacular increase of viscosity and α -relaxation times of fragile glass-formers (almost) entirely to the density changes. It is thus important to evaluate the role of density and temperature in driving the jamming process that leads to the glass transition *at 1 atm*.

Basic models and theories are usually formulated in terms of either density or temperature as control variable, but experiments are carried out with pressure and temperature as external control variables. The data must be converted, when enough experimental results are available, in order to analyze the influence of density at constant temperature and that of temperature at constant density, for a range of density and temperature that is characteristic of the phenomenon *at 1 atm*. Extant analyses [34] are far from exhaustive. However, as illustrated in Fig. 8, the characteristic super-Arrhenius T-dependence of the viscosity, η , and α -relaxation times, τ_α , appears predominantly due to the variation of temperature and not to that of density. This conclusion is confirmed by a comparative study of the contributions induced by density variations (at constant temperature) and by temperature variations (at constant density) to the rate of change of η and τ_α at constant (low) pressure in the viscous liquid regime of several molecular and polymeric glass-formers. [34]

How general is the above result? Temperature appears to be the dominant variable

controlling the viscous super-Arrhenius slowing down of supercooled liquids at low pressure, but this may not be the case at much higher pressure (although not much data are presently available to confirm this point), and it is most likely not true for describing the concentration-driven congestion of dynamics in colloidal suspensions. In the absence of a “super-universal” picture of the jamming associated with glass formation, we shall restrict ourselves, as we have implicitly done above, to the consideration of supercooled liquids at 1 atm.

4. What are the relevant characteristic temperatures?

There is no unbiased way of presenting the phenomenology of glass-forming liquids. Choices must be made about the emphasis put on the different aspects, about the best graphic representations, and about the way in which one analyzes experimental data. To make sense out of the wealth of observations and measurements, it is natural to look for characteristic temperatures about which to organize and scale the data. However, since no singularity is directly detected, the selection of one or several relevant temperatures is far from straightforward. The temperatures that can be easily determined experimentally are the boiling point, T_b , the melting point, T_m , and the glass transition temperature(s), T_g . Unfortunately, the former two are generally considered as irrelevant to the jamming phenomenon, and the latter has an operational rather than a fundamental nature (see the introduction).

Several other candidates have been suggested, that can be split into two groups. First, there are “extrapolation temperatures” *below* T_g , i.e., temperatures dynamically inaccessible to supercooled liquids, at which extrapolated behavior diverges or becomes singular. This is the case of the VFT temperature T_0 (see Eq. 1) and the Kauzmann temperature T_K (see section II-4 and Fig. 4). In the second group are “crossover temperatures” *above* T_g at which a new phenomenon seems to appear (decoupling of rotations and translations, emergence of a secondary β process, etc.), a crossover of behavior or a change of α -relaxation mechanism seems to take place (passage from Arrhenius to super-Arrhenius T -dependence, arrest of the relaxation mechanisms described by the mode-coupling theory, putative emergence of activated barrier crossing processes, etc.). A variety of such temperatures for the fragile glass-former *OTP* are shown in Fig. 9: the location of the different characteristic temperatures is illustrated on an Arrhenius plot of the viscosity. It is interesting to note that most putative crossover behaviors occur in the region of strong curvature where $\eta \sim 1 - 10^2$ Poise or $\tau_\alpha \sim 10^{-10} - 10^{-8}$ sec, while, on the other hand, the temperatures obtained by extrapolation of data to low T lie fairly close to each other, some 40 K below T_g .

5. What can be learned from computer simulations?

Computer simulation studies, [39] in particular those based on Molecular Dynamics algorithms, have proven extremely valuable in investigating the structure and dynamics of simple, ordinary liquids. Their contribution to the understanding of the glass transition is unfortunately limited, the main reason being the restricted range of lengths and times that are accessible to Molecular Dynamics simulations: typical simulations on atomistic models

consider $10^3 - 10^4$ atoms and can follow relaxations for less than 10^{-8} sec (when expressing the elementary time step in terms of parameters characteristic of simple liquids). As a result, the viscous, deeply supercooled regime of real glass-forming liquids, where strong super-Arrhenius behavior, heterogeneous dynamics, and other significant features associated with the jamming process develop, is out of reach, as is the laboratory glass transition that occurs on a time scale of 10^2 or 10^3 sec. Simple liquid models do form “glasses” on the observation, i.e., simulation, time with many of the attributes of the laboratory glass transition: abrupt change in the thermodynamic coefficients, dependence on the cooling rate, aging effects, etc⁵. However, these supercooled simulation liquids are not truly fragile (the T -dependence of the α -relaxation time shows only small departure from Arrhenius behavior) and are not deeply supercooled so that one’s ability to extract insights into the deeply supercooled fragile liquids is questionable.

Computer simulations can be useful in studying the moderately supercooled liquid region, where one can observe the onset of viscous slowing down (see for instance Fig. 9). The major interest of such studies is that static and dynamic quantities that are not experimentally accessible can be investigated, such as multi-body (beyond two-particle) correlations involving a variety of variables and microscopic mechanisms for transport and relaxation. They also allow for testing in detail theoretical predictions made in the relevant window of times and lengths (e. g., those of the mode-coupling theory) and for analyzing properties associated with configurational or phase space (see below).

In addition to the much studied one- or two-component systems of spheres with spherically symmetric interaction potentials, [39] the models investigated in computer simulations can be divided into two main groups: on one hand, more realistic microscopic models for molecular glass-formers that attempt to describe species-specific effects; [40] on the other hand, more schematic systems, coarse-grained representations, [41] lower-dimensional systems [42] or toy-models, [43] that bear less detailed resemblance with real glass-formers, but can be studied on much longer time scales and with bigger system sizes.

IV. THEORETICAL APPROACHES.

There is a large number of theories, models, or simply empirical formulae that attempt to reproduce pieces of the phenomenology of supercooled liquids. There are fewer approaches, however, that address the question of why and how the viscous slowing down leading to the glass transition, with its salient characteristics described in the preceding sections, occurs in liquids as they are cooled. In the following, we shall briefly review the main theoretical approaches, with an emphasis on the concepts and methods that may prove useful in other

⁵ However, these models are effectively high-temperature structures, since they correspond to liquid configurations that are kinetically arrested at a temperature at which the primary relaxation time is of the order only of nanoseconds. Even with systems specially designed to avoid crystallization, such as binary Lennard-Jones mixtures, the cooling rates to prepare glasses (10^8 to 10^9 K/sec) are orders of magnitude higher than those commonly used in experiments.

areas of physics where some sort of jamming process is also encountered⁶. More specifically, we shall discuss phenomenological models based on free volume and configurational entropy, the description of a purely dynamic arrest resulting from mode-coupling approximations, ideas relying on the consideration of the topographic properties of the configurational space (energy and free-energy landscapes) or on the analogy with generalized spin glass models, and approaches centered on the concept of frustration.

1. Free volume

Free-volume models rest on the assumption that molecular transport in viscous fluids occurs only when voids having a volume large enough to accommodate a molecule form by the redistribution of some “free volume”, where this latter is loosely defined as some surplus volume that is not taken up by the molecules. In the standard presentation by Cohen and Turnbull, [46] a molecule in a dense fluid is mostly confined to a cage formed by its nearest neighbors. The local free volume, v_f , is roughly that part of a cage space which exceeds that taken by a molecule. It is assumed that between two events contributing to molecular transport, a reshuffling of free volume among the cages occurs at no cost of energy. Assuming also that the local free volumes are statistically uncorrelated, one derives a probability distribution, $P(v_f)$, which is exponential,

$$P(v_f) \propto \exp\left(-\gamma \frac{v_f}{\overline{v_f}}\right), \quad (4)$$

where $\overline{v_f}$ is the average free volume per molecule and γ is a constant of order 1. Since the limiting mechanism for the diffusion of a molecule is the occurrence of a void, i.e., a local free volume v_f larger than some critical value, v_0 , that is approximately equal to the molecular volume, the diffusion constant D is given by the probability of finding a free volume equal to v_0 ; this leads to an expression for D , and by extension for the viscosity η ,

$$\eta \propto 1/D \propto \exp\left(\gamma \frac{v_0}{\overline{v_f}}\right), \quad (5)$$

which is similar to the formula first proposed by Doolittle. [47]

In the Cohen-Turnbull formulation, the average free volume per molecule is given by $\overline{v_f} = v - v_0$, where $v = 1/\rho$ is the average total volume per molecule. The free-volume concept, in zeroth order, relies on a hard-sphere picture in which thermal activation plays no role. For application to real liquids, temperature enters through the fact that molecules, or molecular segments in the case of polymers, are not truly “hard” and that, consequently, the constant-pressure volume is temperature-dependent,

$$\overline{v_f(T)} \propto \alpha_P(T - T_0), \quad (6)$$

⁶Models addressing more specific questions, such as the “coupling model” [44] or the “continuous time random walk”, approach [45] are discussed in the reviews cited in [1].

where α_P is the coefficient of isobaric expansivity and T_0 is the temperature at which all free volume is consumed, i.e., $v = v_0$. Inserting the above equation in the Doolittle formula, Eq. (4), gives the VFT expression, Eq. (1). An unanswered, but fundamental question associated with Eq. (6) is why the free volume should be consumed at a nonzero temperature, T_0 ? An extended version of the free-volume approach has been developed by Cohen and Grest, in which the cages or “cells” are divided into two groups, liquid-like and solid-like, and concepts from percolation theory are included to describe the dependence upon the fraction of liquid-like cells. [48] (See also the model for molecular diffusivity in fluids of long rod molecules by Edwards and Vilgis. [49])

The main criticisms of the free volume models are (i) that the concept of free volume is ill-defined, which results in a variety of interpretations and difficulty in finding a proper operational procedure even for simple model systems, and (ii) that the pressure dependence of the viscosity (and α -relaxation times) is not adequately reproduced. This latter feature has been emphasized in many studies, [17,34,50] and it is a consequence of the observation made above (see II-3) that the viscous slowing down of glass-forming liquids at 1 atm and more generally at low pressure is primarily controlled by temperature and not by density or volume. Glass formation in supercooled liquids does not predominantly results from the drainage of free volume, but rather from thermally activated processes.

2. Mode-coupling approximations

The theory of glass-forming liquids that has had the highest visibility for more than a decade is the mode coupling theory. [51] It predicts a dynamic arrest of the liquid structural relaxation without any significant change in the static properties. All structural quantities are assumed to behave smoothly and jamming results from a nonlinear feedback mechanism that affects the relaxation of the density fluctuations. Formally, the theory involves an analysis of a set of nonlinear integro-differential equations describing the evolution of pair correlation functions of wave-vector- and time-dependent fluctuations that characterize the liquid. These equations have the form of generalized Langevin equations, and they can be derived by using the Zwanzig-Mori projection-operator formalism. The equation for the quantity of prime interest in the theory, the (normalized) correlation function of the density fluctuations,

$$\phi_Q(t) = \frac{\langle \rho_Q(t) \rho_Q^*(0) \rangle}{\langle |\rho_Q(0)|^2 \rangle}, \quad (7)$$

where $\rho_Q(t) = \sum_j \exp(i\mathbf{Q}\mathbf{r}_j)$ and \mathbf{r}_j denotes the position of the j th particle, can be written as

$$\frac{d^2}{dt^2} \phi_Q(t) + \Omega_Q^2 \phi_Q(t) + \int_0^t dt' m_Q(t-t') \frac{d}{dt'} \phi_Q(t') = 0, \quad (8)$$

where Ω_Q is a microscopic frequency obtainable from the static structure factor, $S(Q) \propto \langle |\rho_Q(0)|^2 \rangle$, and $m_Q(t)$ is the time-dependent memory function that is formally related to the correlation function of a Q -dependent random force. The above equation being exact, the crux of the mode-coupling approach consists in formulating an approximate

expression for $m_Q(t)$. The mode-coupling scheme has been implemented for liquids both in the frame of the kinetic theory of fluids [51] and that of the fluctuating nonlinear hydrodynamics. [52] It essentially boils down to approximating the memory function $m_Q(t)$ as the sum of a bare contribution coming from the fast relaxing variables and a mode-coupling contribution coming from the slowly decaying bilinear density modes,

$$m_Q(t) = \gamma\delta(t) + \sum_{\mathbf{Q}'} V_{\mathbf{Q}\mathbf{Q}'} \phi_{\mathbf{Q}'}(t) \phi_{|\mathbf{Q}-\mathbf{Q}'|}(t), \quad (9)$$

where the vertices $V_{\mathbf{Q}\mathbf{Q}'}$ can be expressed in terms of the static structure factor. The self-consistent solution of the resulting set of nonlinear equations predicts a slowing of the relaxation that is attributed, within a purely homogeneous picture (see II-2), to a cage effect and to the feedback mechanism above mentioned. This solution exhibits a dynamic arrest at a critical point, T_c , which represents a transition from an ergodic to a nonergodic state with no concomitant singularity in the thermodynamics and structure of the system. The main achievements of the mode-coupling approach are the predicted anomalous increase in relaxation time and the appearance of a two-step relaxation process with decreasing temperature, as indeed observed in real fragile glass-formers (compare Fig. 10 to Fig. 7) and in molecular dynamics simulations. [39] Early on, however, it was realized, both from empirical fits to experimental data and from comparison to simulation data on model systems, that the dynamic arrest at T_c did not describe the observed glass transition at T_g nor the transition to an “ideal glass” at a temperature below T_g . This is illustrated in Fig. 11. Thus, the T_c was interpreted as a temperature above T_g . The singularity at T_c is avoided because of the breakdown of the simple mode-coupling approximation, Eq. 9, and the T_c of what is called the “idealized” mode-coupling theory is taken as a crossover below which additional relaxation mechanisms, such as activated processes, presumably take over. Unfortunately, beyond some empirical introduction, [51,52] activated processes are not theoretically described by mode-coupling approaches, and so the theory of α relaxation has not been extended to temperatures below T_c . To draw once again a parallel with critical phenomena (where a singularity occurs at T_c in the structure and the thermodynamics of the system), mode-coupling approximations, as formulated for instance by Kawasaki, are known to describe quite well the standard critical slowing down, but not the activated dynamic scaling such as that observed in the random field Ising model (see section I-1). This failure is related to the underlying nature of the approximation that corresponds to a one-loop self-consistent resummation scheme in a perturbative treatment [52,54] (see also below in III-4 the parallel with spin glass models).

Mode-coupling approaches can thus describe at best the dynamics of moderately supercooled liquids⁷ (see Fig. 11). Because of the many detailed predictions it makes in this regime, the mode-coupling theory has stimulated the use and the development of experimental techniques, such as neutron and depolarized light scattering, and molecular dynamics simulations that are able to probe the early stage of the viscous slowing down; but, the very fact that the predicted dynamic singularity is not observed makes it difficult to reach any

⁷It is possible that they are also applicable to the fast- β relaxations even below T_c . [51]

clear-cut conclusion about the quantitative adequacy of the theory, and this has led to much debate in recent years. [55]

3. Configurational entropy and (free) energy landscape

The existence of a crossover temperature in the moderately supercooled liquid region where α -relaxation times are of the order of 10^{-9} sec (hence in the same region as the T_c predicted by the mode-coupling theory) was advocated 30 years ago by Goldstein. [56] Goldstein argued that below this crossover flow is dominated by potential energy barriers that are high compared to thermal energies and slow relaxation occurs as a result of thermally activated processes taking the system from one minimum of the potential energy hypersurface to another. The idea that molecular transport in viscous liquids approaching the glass transition could be best described by invoking motion of the representative state point of the system on the potential energy hypersurface had also been suggested by Gibbs. [57] In his view, the slowing down of relaxations with decreasing temperature is related to a decrease of the number of available minima and to the increasing difficulty for the system to find such minima. The viscous slowing down would thus result from the decrease of some “configurational entropy” that is a measure of the number of accessible minima. These two concepts, potential energy hypersurface, also denoted “energy landscape”, and “configurational entropy”, have gained a renewed interest in recent years, boosted by the analogy with the situation encountered in several generalized spin glass models (see below).

The Adam-Gibbs approach [58] represents a phenomenological attempt to relate the α -relaxation time of a glass-forming liquid to the “configurational entropy”. In the picture, α -relaxation takes place by increasingly cooperative rearrangements of groups of molecules. Any such group, called a “cooperatively rearranging region”, is assumed to relax independently of the others. It is a kind of long-lived heterogeneity. Molecular motion is activated and the effective activated free energy is equal to the typical energy barrier per molecule, which is taken as independent of temperature, times the number of molecules that are necessary to form a cooperatively rearranging region whose size permits a transition from one configuration to a new one independently of the environment. This latter number goes as the inverse of the configurational entropy per molecule, $S_c(T)/N$, where N is the total number of molecules in the sample. Since S_c decreases with decreasing temperature, the reasoning leads to an effective activation free energy that grows with decreasing temperature, i. e., to a super-Arrhenius behavior,

$$\tau_\alpha = \tau_0 \exp \left(\frac{C}{TS_c(T)} \right), \quad (10)$$

where C is proportional to N times the typical energy barrier per molecule. If the configurational entropy vanishes at a nonzero temperature, an assumption somewhat analogous to that in Eq. (6) for the free volume model, but one that is inherent for instance in the Gibbs-di Marzio approximate mean field treatment of a lattice model of linear polymeric chains, [59] then the α -relaxation times diverge at this same nonzero temperature. In particular if the configurational entropy is identified as the entropy difference between the supercooled liquid

and the crystal⁸, the Adam-Gibbs theory allows one to correlate the extrapolated divergence of the α -relaxation times with the Kauzmann paradox (see I-4): the Kauzmann temperature T_K would then signal a singularity both in the dynamics and in the thermodynamics of a supercooled liquid⁹. Note also that by using a hyperbolic temperature dependence to fit the experimental data on the heat capacity difference between the liquid and the crystal, $\Delta C_P(T) = K/T$, and using this formula to extrapolate the configurational entropy down to the Kauzmann temperature, one converts Eq. (10) to a VFT formula,

$$\tau_\alpha = \tau_0 \exp \left(\frac{CT_K}{K(T - T_K)} \right), \quad (11)$$

with the VFT temperature T_0 equal to the Kauzmann temperature T_K . When comparing to experimental data, the configurational-entropy based expressions provide a good description at least over a restricted temperature range, but the resulting estimates for the critical number of molecules composing a cooperatively rearranging region is often found to be unphysically small (only a few molecules at T_g). [1]

Building upon the early suggestion made by Goldstein, [62] and others proposed that the apparent passage with decreasing temperature from flow dynamics described by a mode-coupling approach to activated dynamics such as pictured by the configurational-entropy theory of Adam and Gibbs could be rationalized by considering the physics of exploration of the energy landscape: see Fig. 12. The energy landscape is the potential energy in configurational space. It can be envisaged as an incredibly complex, multi-dimensional ($3N$ dimensions for a system of N particles) set of hills, valleys, basins, saddle-points, and passage-ways around the hills. At constant volume and constant number of particles, this landscape is independent of temperature. However, the fraction of space that is statistically accessible to the representative state point of the system decreases with decreasing temperature, and the system becomes constrained to deeper and deeper wells. (Recall that below the melting point the deepest energy minima corresponding to the crystalline part of configurational space must be excluded when studying the supercooled liquid.) At low enough temperature, when the representative point of the supercooled liquid is mostly found in fairly deep and narrow wells, it seems reasonable to define a “configurational entropy” that is proportional to the logarithm of the number of minima that are accessible at a given temperature. The liquid configurations corresponding to these accessible minima have been called “inherent structures” and Stillinger and coworkers have devised a gradient-descent mapping procedure to find the inherent structures and study their properties in computer

⁸This phenomenological choice for the entropy of configuration has been criticized by Goldstein who showed for several glass-formers that only half of the entropy difference between the liquid and the crystal comes from strictly “configurational” sources; the remainder comes mostly from changes in vibrational anharmonicity or differences in the number of molecular groups able to engage in local motions. [60]

⁹A recent careful, but conjectural analysis of dielectric relaxation data suggests that these data are consistent with the existence of a critical point, both structural and dynamical, at the approximate T_0 specified by the VTF expression in Eq. (1). [61]

simulations. [63] Interestingly, Stillinger has also shown, with fairly general arguments, that if one is to use the above defined notion of configurational entropy, an “ideal glass transition” of the type commonly associated with the Kauzmann paradox, i. e., one characterized by the vanishing of the configurational entropy at a nonzero temperature, cannot occur for systems of limited molecular weight and short-range interactions. [64]

It may be more fruitful to investigate in place of the potential energy landscape a free-energy landscape. Such a landscape can only be defined if one is able to construct a free-energy functional by a suitable coarse-graining procedure, as can be done for instance in the case of mean-field spin glass models (see below). A free-energy landscape is temperature-dependent, and it is important to note that the “configurational entropy”, also called “complexity”, [65] that one can define from the logarithm of the number of accessible free-energy minima differs from the “configurational entropy” computed from the potential energy landscape. In particular, the behavior of the complexity is not restricted by the Stillinger arguments given above.

The “landscape paradigm” is very appealing in rationalizing many observations on liquids and glasses and, more generally, in establishing a framework to describe qualitatively slow dynamics in complex systems that span a wide range of scientific fields. [66] It has been used to motivate, in addition to the Adam-Gibbs theory and other phenomenological approaches like the soft-potential model, [67] simple stochastic models of transport based on master equations. [68] Nevertheless, it has not so far offered a way for elucidating the *physical* mechanism that is responsible for the distinctive features of the viscous slowing down of supercooled liquids.

4. Analogy with generalized spin glass models

If one takes seriously the observation that the extrapolated temperature dependence of both the viscosity (and α -relaxation times) and the “configurational” entropy (taken as the difference of entropy between the liquid and the crystal) become divergent or singular at essentially the same temperature $T_0 \simeq T_K$ (see Fig. 9), one is naturally led to postulate the existence at this temperature of an underlying thermodynamic transition, usually referred to as the “ideal glass transition”. Looking for analogies with phase transitions in spin glasses is then appealing. However, the kind of dynamic activated scaling that would be required to describe the slowing down of relaxations when approaching the ideal glass transition (see I-1) is not found in the most studied Ising spin glasses. [69] Kirkpatrick, Thirumalai, and Wolynes argued that generalized spin glass models, such as Potts glasses and random p -spin systems, would be better candidates. [70,71] The random p -spin model, for instance, is defined by the following hamiltonian:

$$H = \sum_{i_1 < i_2 < \dots < i_p} J_{i_1 i_2 \dots i_p} \sigma_{i_1} \sigma_{i_2} \dots \sigma_{i_p}, \quad (12)$$

where the σ_i ’s are Ising variables and the couplings $J_{i_1 i_2 \dots i_p}$ ’s are quenched independent random variables that can take positive and negative values according to a given probability distribution. The behavior of these systems, *at least when solved in the mean-field limit where the interactions between spins have infinite range*, bears many similarities with the theoretical description of glass-forming liquids outlined above. Indeed, mean-field Potts

glasses (with a number of states strictly larger than 4) and mean-field p -spin models (with $p \geq 3$) have essentially the following characteristics:

- (i) At high temperature, the system is in a fully disordered (paramagnetic) state. At a temperature T_D , there appears an exponentially large number of metastable “glassy” states whose overall contribution to the partition function is equal to that of the paramagnetic minimum. The free energy and all other static equilibrium quantities are fully regular at T_D , but the dynamics have a singularity of the exact same type as that found in the mode-coupling theory of liquids. At T_D , the system is trapped in one of the metastable free-energy minima, and ergodicity is broken.
- (ii) Below T_D , a peculiar situation occurs. The partition function has contributions from, both, the paramagnetic state and the exponentially large number of “glassy” (free-energy) minima, the logarithm of which defines the configurational entropy or complexity. This latter decreases as the temperature is lowered.
- (iii) At a nonzero temperature $T_s < T_D$, the configurational entropy vanishes. The system undergoes a *bona fide* thermodynamic transition to a spin-glass phase. The transition has been termed “random first order” [70,71] because it is second-order in the usual thermodynamic sense (with, e. g., no latent heat), but shows a discontinuous jump in the order parameter. (Technically, within the replica formalism, it corresponds to a one-step replica symmetry breaking with a discontinuous jump of the Edwards-Anderson order parameter. [69–71])

These mean-field systems are the simplest, analytically tractable models found so far that display a high-temperature mode-coupling dynamic singularity, a nontrivial free-energy landscape, and a low-temperature ideal (spin) glass transition with an “entropy crisis”¹⁰. Analyzing them sheds light on the mode-coupling approximation, whose validity for fluid systems is otherwise hard to assess. The mode-coupling approximation becomes exact in the mean-field limit, because the barriers separating the metastable minima diverge (in the thermodynamic limit) at and below T_D as a result of the assumed infinite range of the interactions. One expects that in a finite-range model, provided the same type of free-energy landscape is still encountered, barriers are large but finite and ergodicity is restored by thermally activated processes. Accordingly, the dynamic transition is smeared out, and the activated relaxation mechanisms that take over must be described in a nonperturbative way, as suggested for instance by Kirkpatrick, Thirumalai, and Wolynes [71] in their dynamic scaling approach based on entropic droplets.

An advantage of an analogy between glass-forming liquids and generalized spin glasses¹¹ is that the powerful tools that have been developed in the theory of spin-glass models to characterize the order parameter and the properties associated with the existence of a large number of metastable glassy states, among which the replica formalism, [69] can be used

¹⁰They are also aging phenomena, as discussed in Ref [5].

¹¹See also the frustrated percolation model [72].

mutatis mutandis to study liquids and glasses. [73] However, to make the analogy really successful, one must still find a short-range model (even more convincing would be a model without quenched disorder) that actually displays activated dynamic scaling and a random first-order transition and make progress in describing the slow relaxation.

5. Intrinsic frustration without randomness

Spin glasses, and related systems like orientational glasses, vortex glasses and vulcanized matter, [74] owe their fascinating behavior to two main ingredients: *randomness*, namely the presence of an externally imposed quenched disorder, and *frustration*, which expresses the impossibility of simultaneously minimizing all the interaction terms in the energy function of the system. Liquids and glasses (sometimes called "structural glasses" to stress the difference with spin glasses) have no quenched randomness, but frustration has been suggested as a key feature to explain the phenomena associated with glass formation. [75–79] Frustration in this context is attributed to a competition between a short-range tendency for the extension of a locally preferred order and global constraints that preclude the periodic tiling of the whole space with the local structure.

The best studied example of such an intrinsic frustration concerns single-component systems of spherical particles interacting with simple pair potentials. What is usually called "geometric" or "topological" frustration can be more easily understood by comparing the situations encountered in 2 and 3 dimensions [76] (see Fig. 13). In 2 dimensions, the arrangement of disks that is locally preferred, in the sense that it maximizes the density and minimizes the energy, is a hexagon of 6 disks around a central one, and this hexagonal structure can be extended to the whole space to form a triangular lattice. In 3 dimensions, as was shown long ago by Frank, [80] the locally preferred cluster of spheres is an icosahedron; however, the 5-fold rotational symmetry characteristic of icosahedral order is incompatible with translational symmetry, and formation of a periodic icosahedral crystal is forbidden. Geometric or topological frustration is thus absent in the 2-dimensional case but present in the 3-dimensional case. A consequence of this, for instance, is that crystallization is continuous, or weakly first-order, in 2 dimensions (with some subtleties related to ordering in 2 dimensions [81]) whereas it is strongly first-order in 3 dimensions and accompanied by the breaking of the local icosahedral structure to make the face-centered-cubic or hexagonal-close-packed order that allows to tile space periodically. (In contrast, aligned cubes in 3 dimensions have no frustration and undergo a continuous freezing transition to a crystalline state. [82]). The geometric frustration that affects spheres in 3-dimensional Euclidean space can be relieved in curved space with a specially tuned curvature; the creation of topological defects (disclination lines) can then be viewed as the result of forcing the ideal icosahedral ordering into "flat" space. This picture of sphere packing disrupted by frustration has been further developed in models for simple atomic systems and metallic glasses, [75,76] and the slowing down of relaxations has been tentatively attributed to the topological constraints that hinder the kinetics of the entangled defect lines; [76] however, the treatment remains only qualitative and incomplete.

A significant difficulty in applying the concept of geometric or topological frustration to supercooled liquids is that real fragile glass-formers are in general either mixtures or single-component systems of nonspherical molecules with a variety of shapes, all of which obscures

the detailed mechanisms and constraints that are responsible for the frustration. Attempts have been made to get around this problem by proposing a more coarse-grained description of frustration¹². [77–79]

In Stillinger’s ”tear and repair” mechanism for relaxation and shear flow [78] and in the more recently introduced ”frustration-limited domain theory”, [79] frustration is described as the source of a strain free energy that opposes the spatial extension of the locally preferred structure and grows super-extensively with system size. It results in the breaking up of the liquid into domains, whose size and growth with decreasing temperature are limited by frustration, the weaker the frustration the larger the domains. The super-Arrhenius temperature dependence of the viscosity and α -relaxation times and the heterogeneous nature of the dynamics are attributed to these domains (see also Ref. [77]). Progress has been made along these lines, by making use of a scaling approach based on the concept of avoided critical behavior¹³. [79,84] However, the putative order variable characterizing the locally preferred structure of the liquid has not yet been properly identified, and, as in the case of the generalized spin-glass models discussed above, one must still give convincing evidence that the 3-dimensional statistical-mechanical frustrated models that have been suggested as minimal theoretical descriptions do show the expected activated dynamics.

V. CONCLUSION

The viscous slowing down of supercooled liquids that leads to glass formation can be considered as a classical and thoroughly studied example of a ”jamming process”. In this review, we have stressed the distinctive features characterizing the phenomenon: strong, super-Arrhenius temperature dependence of the viscosity and the α -relaxation times, non-exponential and heterogeneous character of the α relaxation, absence of marked changes in the structural (static) quantities, rapid decrease of the liquid entropy relative to that of the crystal, appearance of a sequence of steps (or regimes) in the relaxation functions. These features are common to most glass-forming liquids (with the exception of systems forming 2- and 3-dimensional networks of strong intermolecular bonds). We have also discussed the main theoretical approaches that have been proposed to describe the origin and the nature of the viscous slowing down and of the glass transition. We have emphasized the concepts,

¹²In addition, several ”toy models” possessing frustration, but no quenched disorder have been studied by computer simulation: see for instance Ref. [83].

¹³This approach differs from both those based upon spin-glass analogies and those in which the slow kinetics are attributed to frustration-induced entangled defect lines in that these others scale about a low-temperature characteristic point signifying ultimate slowing down, whereas in the frustration-limited domain theory the scaling is carried out about a high-temperature characteristic point signifying the initiation of anomalously slow dynamics. For the same reason, it also differs from the domain (or cluster) picture that has been proposed on the basis of an analogy between a supercooled liquid approaching the glass transition and a mean-field model with purely repulsive interactions near its spinodal. [85]

such as free volume, dynamic freezing and mode-coupling approximations, configurational entropy and (free) energy landscape, and frustration, that could be useful in other areas of physics where jamming processes are encountered.

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FIGURES

FIG. 1. Super-Arrhenius T -dependence of the viscosity η and α -relaxation times τ_α in glass-forming liquids. **a)** Logarithm (base 10) of η and τ_α versus reduced inverse temperature T_g/T for several liquids. For GeO_2 , a system forming a network of strong intermolecular bonds, the variation is almost linear, whereas the other liquids (glycerol, m-toluidine, and ortho-terphenyl) are characterized, below some temperature T^* , by a strong departure from linear dependence: the behavior is nearly Arrhenius in the former case and super-Arrhenius in the latter. (Data taken from references cited in Ref. [8] and from C. Alba-Simionesco, private communication.) **b)** Effective activation free energy $E(T)$, obtained from data shown in **a)**, as a function of inverse temperature. Both $E(T)$ and T are divided by the crossover temperature T^* shown in **a)**.

FIG. 2. Imaginary part of the dielectric susceptibility χ'' of liquid m-toluidine versus $\log_{10}(\omega)$ for several temperatures close to T_g ($T_g = 183.5K$). The inset shows that the α peak is broader than a Debye spectrum that would correspond to a purely exponential relaxation in time. (Data from C. Tschirwitz, E. Rössler, and C. Alba-Simionesco, private communication.)

FIG. 3. Static structure factor $S(Q)$ of liquid (deuterated) ortho-terphenyl at several temperatures from just below melting ($T_m = 329K$) to just above the glass transition ($T_g = 243K$). The inset shows the weak variation with temperature of $S(Q)$ for three values of Q indicated by the symbols above the Q -axis. (From Ref. [13].)

FIG. 4. Kauzmann's representation of the "entropy paradox": entropy difference ΔS between the liquid and the crystal (normalized by its value ΔS_m at the melting point) versus reduced temperature T/T_m . The break in the slopes of the full lines signals the glass transition at T_g . The dashed lines indicate an extrapolation of the entropy difference curves below T_g . Except for the strong, network-forming liquid B_2O_3 , the extrapolated entropy difference vanishes at a nonzero temperature T_K . (Data from Refs. [16], [18], and from H. Fujimori and C. Alba-Simionesco, private communication.)

FIG. 5. Time dependence of the (normalized) dynamic structure factor $S(Q,t)/S(Q)$ of liquid $Ca_{0.4}K_{0.6}(NO_3)_{1.4}$ (for $Q \simeq 1.9\text{\AA}^{-1}$) at various temperatures. The continuous lines are obtained by Fourier transforming neutron time-of-flight data and the symbols represent neutron spin-echo results. When T decreases, two steps separated by a plateau appear in the relaxation. (From Ref. [19].)

FIG. 6. Scaling plot for the imaginary part χ'' of the dielectric susceptibility of several glass-forming liquids (glycerol, salol, propylene glycol, dibutyl-phtalate, α -phenyl-o-cresol, ortho-terphenyl, ortho-phenylphenol). Experimental data similar to those shown in Fig. 2, but for 13 decades of frequency, are collapsed for all temperatures and all liquids onto the master-curve $w^{-1}\log_{10}(\chi''\omega_\alpha/\Delta\chi\omega)$ vs $w^{-1}(1+w^{-1})\log_{10}(\omega/\omega_\alpha)$; ω_α is the α -peak position, w is a shape factor that characterizes the deviation from Debye behavior, and $\Delta\chi$ is the static susceptibility. (From Ref. [11].)

FIG. 7. “Decoupling” between rotational and translational time scales: logarithm (base 10) of the rotational (D_r) and translational (D_t) diffusion coefficients for ortho-terphenyl as a function of temperature and viscosity. D_r (diamonds) follows the viscosity at all temperatures whereas D_t (squares, triangles, and dots) departs from viscosity (and from D_r) below $T \simeq 290K$. (From Ref. [28]).

FIG. 8. Relative influence of temperature (T) and density (ρ) on the viscous slowing down of liquid triphenyl phosphite. **a)** $\log_{10}(\eta)$ versus ρ at constant T for several isotherms. Also shown are the isobaric data at $P = 1atm$ (under atmospheric pressure, the glass transition takes place at $T_g \simeq 200K$ and $\rho_g \simeq 1.275g/cm^3$). **b)** $\log_{10}(\eta)$ versus T at constant ρ for several isochores. Note that the change of viscosity is much smaller with density (at constant T) than it is with temperature (at constant ρ) for the range of temperature and density characteristic of the liquid and supercooled liquid phases at atmospheric pressure. (From Ref. [34].)

FIG. 9. Illustration of the various choices of characteristic temperature for describing the viscous slowing down of liquid ortho-terphenyl. $\log_{10}(\eta)$ is plotted versus inverse temperature. “Extrapolation” temperatures: $T_0(VFT, \text{ see Eq. 1}) = 200 - 202K$ [18,35], T_K (Kauzmann, see I-4)=204K [18]. “Crossover” temperatures: T^* (see Fig. 1 and III-5)=350K [8], T_c (MCT, see III-2)=276 - 290K [38], $T_A = 455K$ [36], $T_B = 290K$ [37], $T_X = 289K$ [37]. Also shown are the experimentally measured boiling ($T_b = 610K$), melting ($T_m = 311K$), and glass transition ($T_g = 246K$) temperatures. (Viscosity data from Ref. [38].)

FIG. 10. Mode-coupling scenario of kinetic freezing and appearance of a 2-step relaxation: time dependence of the (normalized) density-density correlation function for a schematic mode-coupling model. The curves from A to G correspond to the approach toward the dynamic singularity from the ergodic state. The other curves correspond to the nonergodic state. (From Ref. [51].)

FIG. 11. Breakdown of the “idealized” mode-coupling theory illustrated on $\log_{10}(\eta)$ versus $1/T$ for liquid ortho-terphenyl (see caption to Fig. 9). The continuous line is the mode-coupling fit to the experimental data. The predictions break down below a point at which the viscosity is of the order of 10 Poise; the dynamic singularity is not observed, and T_c is interpreted as a crossover temperature.

FIG. 12. Illustration of the putative relation between the rapid increase of α -relaxation time (**a**), the decrease of the entropy difference between the liquid and the crystal (**b**), and the characteristic energy level on the (schematic) potential energy landscape (**c**) for a fragile glass-former at various temperatures. The ideal glass level corresponds to the Kauzmann temperature (see I-4) and to an extrapolated divergence of the relaxation time; Goldstein’s crossover (see III-3) takes place somewhat below point 2. (From Ref. [17].)

FIG. 13. Illustration of geometric frustration for spherical particles. **a)** Packing in 2 dimensions: equilateral triangles are preferred locally and combine to form a hexagonal local cluster that can tile space to generate a close-packed triangular lattice. **b)** Packing in 3 dimensions: tetrahedra are preferred locally and combine (with slight distortions) to form a regular icosahedral cluster; however, the 5-fold symmetry axes of the icosahedron preclude a simple icosahedral space-filling lattice. (From Ref. [76].)











